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(54) Title: HIGH FREQUENCY INDUCTION PLASMA METHOD AND APPARATUS

(57) Abstract

A method and apparatus for generating plasmas for chemical vapor deposition, etching, etc., and particularly for the deposition of large-area diamond films, comprising a chamber (10) defined by a base plate (12), canopy (14) and O-ring (16). The sidewalls surrounding the longitudinal axis (20) of the chamber are encircled by an axially-extending array of current-carrying conductors (not shown) that are substantially transverse to the longitudinal axis. A gas is provided to the chamber and exhausted by a port (19). A high-frequency current is produced in the conductors to magnetically induce ionization of the gas in the chamber and form a plasma sheath that surrounds and extends along the longitudinal axis, conforming to the sidewalls of the chamber. A work surface extending in the direction of the longitudinal axis of the chamber is positioned adjacent a sidewall, exposed to the plasma sheath and treated by the plasma.

TITLE OF THE INVENTION

HIGH FREQUENCY INDUCTION PLASMA METHOD AND APPARATUS

BACKGROUND OF THE INVENTION

Field of the Invention

The instant invention relates to apparatus and methods for generating intense plasmas adapted for chemical vapor deposition, etching and other operations. In one important embodiment, the invention relates to a vapor deposition system in which a plasma is used to deposit large-area diamond films.

Discussion of Background

Prior art chemical vapor deposition (CVD) processes for the production of diamond films include DC torch, microwave, hot filament and rf plasma techniques. To date, film costs have been exceedingly high. Most of the prior techniques deposit diamond films only over small areas, which slows production and limits applicability of the films; and the rates at which film is deposited are low. The combination of small deposition area and slow deposition rates causes a high cost of production for the films.

SUMMARY OF THE INVENTION

The present invention provides apparatus and methods for treating large areas at fast rates with an intense plasma. In brief summary, a method of the invention comprises

a) providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis;

b) providing an axially-extending array of current-carrying conductors that at least partially encircle the chamber and are substantially transverse to the longitudinal axis;

c) providing gaseous material in the chamber;

d) providing a high-frequency current in the conductors to magnetically induce ionization of the gaseous material in the chamber and form a plasma sheath that surrounds the

longitudinal axis and conforms to sidewalls of the chamber;
and

        e)   exposing to the plasma sheath a work surface that
extends in the direction of the longitudinal axis.

        The chamber generally has at least one large-area planar
sidewall, and the plasma sheath extends over the sidewall,
parallel to the sidewall. Also, the current-carrying
conductors preferably comprise conductor loops electrically
connected in parallel to minimize impedance in the circuit and
thereby maximize the applied current in the conductors that
generate a magnetic field in the chamber.   To further achieve
low impedance, at least part of the individual conductor loops
are generally comprised of large-diameter high-conductivity
rods, which preferably are tubular to allow cooling of the
conductors.

        To prepare diamond film, the gaseous material introduced
into the chamber comprises diamond-precursor ingredients such
as a mixture of vapors of water and alcohol or hydrogen and
methane. Diamond film is deposited in the reactor at
volumetric production rates per unit of power input that,
insofar as known to us, are higher than those reported for any
other diamond-forming vapor deposition techniques; and very
large-area diamond films may be deposited.

        The method can be practiced on apparatus that comprises

        a chamber having a longitudinal axis and sidewalls
that surround and extend parallel to the longitudinal axis, at
least one sidewall being an extensive planar wall that is
parallel to the longitudinal axis;

        means for providing a gas in the chamber;

        an axially extending array of current-carrying
conductor loops that are substantially transverse to the
longitudinal axis, at least partially encircle the chamber,
and establish a magnetic field within the chamber parallel to
the longitudinal axis of the chamber; and

        a high-frequency power supply connected to the
conductor array and adapted to provide high-frequency current

to the conductor loops to magnetically induce ionization of
the gaseous material in the chamber.

Although the conductor loops can be electrically
connected in series, as in a helical wire, preferably the
conductor loops are electrically connected in parallel, and
comprise at least in part cooled copper tubes.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of
the attendant advantages thereof will be readily obtained as
the same becomes better understood by reference to the
following detailed description when considered in connection
with the accompanying drawings, wherein:

FIG. 1 is a perspective view of a chamber useful in the
present invention.

FIG. 2 is an end view of the chamber of FIG. 1.

FIG. 2a is a sectional view along the lines 2a - 2a in
FIG 2 in which the tube 18a is shown enlarged and not drawn to
scale for purposes of illustration.

FIG. 3 is a perspective view of another embodiment of a
chamber useful in the invention.

FIG. 3a is a sectional view along the lines 3a - 3a in
FIG. 3.

FIG. 4 is a perspective view of an axially extending
array of current-carrying conductors, together with a diagram
of a power supply useful in the invention.

FIGS. 5 (a) to (e) depict in schematic top views various
arrangements of current-carrying conductors useful in the
present invention, and FIG 5(f) depicts in side view another
arrangement.

FIG. 6 is a diagram of another power supply useful in the
present invention.

FIG. 7 is a perspective diagram of another chamber useful
in the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, wherein like reference numerals designate identical or corresponding parts throughout the several views, and more particularly to Figures 1, 2 and 2a thereof, an illustrative pressure-controlled chamber 10 for use in apparatus of the present invention includes a substantially planar base plate 12 and a canopy portion 14. An O-ring 16 is typically interposed between the base plate 12 and the canopy portion 14 to effect a seal between these elements. When the chamber 10 is partially evacuated, atmospheric pressure forces the base plate 12 and the canopy portion 14 together. Tube 19 is fused to one end of the canopy portion 14 and serves as a vacuum exhaust port. A smaller-diameter inlet tube 18 is supported coaxially within the tube 19 and extends into the approximate center of the chamber 10, whereby various reactant gases are introduced to the chamber 10. In one preferred variation, as shown in Figure 2a, circular openings 18a near the end of the inlet tube 18 allow gas to be distributed more uniformly in the chamber and thereby contribute to a more uniform treatment or deposit on a work surface in the chamber. Alternatively to the illustrated coaxial arrangement, inlet tube 18 and outlet tube 19 may be placed at opposite ends of the chamber. The longitudinal axis 20 of the chamber is parallel to the desired direction of the applied magnetic field in the chamber.

The chamber is preferably formed from dielectric material such as, for example, quartz, ceramics, plastics, composite materials, and the like. Dielectric material allows magnetic and electric field penetration into the chamber. The base plate 12 and canopy portion 14 in the construction shown in Figure 1 preferably have a wall thickness of about 1 cm to about 5 cm, more preferably about 2 cm to about 3 cm. Base plate 12 can have any plan-view shape, for example, square, rectangular, round, oval, ellipsoidal, or irregular, adapted to mate with the canopy. Canopy 14 of chamber 10 can be any shape which provides containment of the low pressure

atmosphere in chamber 10 and has structural integrity, e.g.,
to limit the effect of atmospheric pressure when the interior
of the chamber is at low pressure and heated.   Canopy 14 can
be, for example, dome shaped, hemispherical, or rectangular;
in the latter case, for example, it might comprise a flat
panel that matches and is parallel to base plate 12, with
walls extending between base plate 12 and the flat panel.

     Chambers used in the invention preferably have at least
one extensive substantially planar surface which serves as a
work surface or supports a work surface.   In the chamber 10,
the base plate 12 is such a planar surface.   In addition, the
base plate 12 is flat, but could be configured, e.g., with a
network of ridges.   Such configured surfaces are regarded as
planar herein, since the length and width of the surfaces is
far greater than any thickness or height dimension.   The
larger the planar surface, the larger the area of a planar
film that can be deposited or the larger the planar surface
that can be treated.   The planar surface is preferably at
least 100 cm^2 in area and more preferably 500 cm^2 or larger,
e.g., 1 or 2 m^2 in area or larger.

     In a different embodiment of the present invention,
shown in FIG. 3, base plate 12´ is substantially flat, and
canopy 14´ is semicylindrical in form.   The plate 12´ and
canopy 14´ can be both made of quartz and be fused together.
Endplate 13 further defines chamber 10´ with sealing achieved
by O-ring 15 against glass plate 17, which is fused to the
base plate 12´ and canopy 14´ .   A second endplate, 21´, is
at the other end of chamber 10´.   Endplate 13 is provided with
inlet port 18´ while the endplate 21 is provided with an
outlet port 19´.

     As previously stated, a rectangular chamber can be used
as generally shown in FIG. 7.   A rectangular chamber is
preferred for some applications, because a large-area planar
film can be deposited on both the large-area sidewalls of the
chamber (top and bottom walls in FIG. 7), as well as on the
shorter sidewalls extending between the large-area sidewalls.

"Sidewalls" refers to walls that extend in the direction of
the longitudinal axis (though they may at the same time extend
toward the longitudinal axis, as in the case of two of the
slanted portions of the dome-shaped canopy 14 of the chamber
10 shown in Figs. 1-2a). The sidewalls surround the
longitudinal axis in that they form the lateral portions of
the enclosure or chamber through which the longitudinal axis
extends; typically the sidewalls are parallel to and spaced
from the longitudinal axis, though as in the case of the noted
two slanting portions of the canopy 14, they may intersect the
longitudinal axis.

   The size of a chamber useful in the invention is limited
only by the mechanical integrity necessary to withstand the
atmospheric pressure applied to the outside of the chamber and
a need for the chamber to be substantially shorter than the
characteristic wavelength at the operating frequency. At 10
MHz, the characteristic wave length is about 30 meters. The
aspect ratio, i.e., the ratio of the width to the height of
the chamber preferably is at least about 2:1, more preferably
at least about 5:1, most preferably about 10:1 or larger.

   The chamber is preferably capable of maintaining an
internal pressure of less than about 100 Torr, more preferably
less than about 10 Torr, most preferably about one Torr or
less. Means for controlling the pressure in the chamber, not
shown, can include, for example, butterfly control valves,
mass flow controllers, and vacuum pumps, and a pressure
measuring device, such as a capacitance manometer, all of
which is well known to those skilled in the art.

   An optional water jacket, not shown, may be included,
having a variety of configurations as are well known to those
skilled in the art of thermal management. The water jacket,
when present, preferably surrounds and cools the chamber which
can reach elevated temperatures at high applied power levels.

   FIG. 4 shows an illustrative power applicator 22, or
antenna, which generally encircles or surrounds the low-
pressure chamber and applies plasma-generating power to the

gaseous contents of the chamber.   Within the chamber the magnetic field is more uniform and intense in comparison to the magnetic field generated by the applicator outside the chamber.   The applicator comprises current-carrying conductors 24, resonated by a capacitor bank comprising capacitors 26.   There may or may not be one capacitor for each conductor 24, depending on the total capacitance needed and the power level to be applied.   In combination, an individual conductor 24 and the capacitor bank to which it is connected form a conductor loop, and the individual conductor loops are electrically connected in parallel through bus bars 38 and 39.

The applicator 22 is shown separate from a chamber for convenience, but the chamber generally lies within the conductor loops, with the longitudinal axis of the chamber substantially perpendicular to the plane of the individual loops.

The "U" - shape for conductors 24 is desirable for enclosing chambers that are more wide than high, as useful for large-area planar depositions. The conductors are desirably of a large diameter so as to minimize impedance. To carry out the invention, current flow is induced in the plasma gas, producing heating, ionization, and dissociation of the gas. The magnitude of the current flow in the plasma gas is proportional to the current flow in the current-carrying conductors. For any current-carrying-conductor, there is an impedance to current flow which increases with the resistance of the chosen conductor and which increases with ωL, where ω = 2 rf and f is the operating frequency and L is the inductance. To maximize current flow for any given applied voltage level requires that high conductivity materials be chosen and that the inductance of the current-carrying-conductors be kept low. Such a condition is achieved in the apparatus shown in Figure 4 where large-diameter conductors are used, and the conductors are arranged as individual loops electrically connected in parallel and arrayed along the longitudinal axis of the chamber.

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The conductors are preferably formed from high
conductivity metals (e.g., silver, copper, aluminum, or brass)
to reduce power loss. As a practical matter, copper or
silver-plated copper is generally used, but silver-plated
brass or aluminum can also be used. Tubes are desirable to
allow cooling fluid to circulate within the conductors. Tubes
having a diameter as low as about 0.5 to 1 cm are useful for
low-power applications, and as high as about 2.5 cm (one inch)
or higher for high-power applications. Solid elements such as
low-resistivity metal strapping, preferably 0.5 cm to 1 cm
wide, more preferably 2 to 5 cm wide, can also be used,
providing proper cooling can be provided, as with fins or
cooling tubes welded to the strapping.

A bus bar, not shown, may be connected across the
midpoint of the length 24a of the conductors 24 and connected
to ground, thereby establishing a symmetrical voltage about a
ground reference, should this be desired. A ground connection
may be provided to reference any part of the application to
ground as well known in the art to achieve either symmetrical
or asymmetrical voltages about a ground reference.

The conductor loops are substantially transverse to the
longitudinal axis of the chamber. In Figure 4, the planes of
the conductor loops are perpendicular to the longitudinal axis
and evenly spaced. In other configurations the conductors can
be spaced irregularly as shown in FIG. 5(b) and (c), e.g., to
achieve desired plasma configurations and intensities.
Chevron configurations as shown in FIG. 5(e) or combinations
of parallel and chevron configurations as shown in FIG. 5(d),
can be used. Also multiple current-carrying conductors, with
one conductor loop overlying or surrounding another as shown
inside view in FIG. 5(f), may be used.

Series-wound coils such as helical coils, preferably
wound as a rectangular or square helix, may also be used. The
higher inductance of such series-wound coils may limit the
current flow in current-carrying conductors and thereby

restrict the maximum value of transferred power; but otherwise such coils would be useful at power levels below the maximum.

The current-carrying conductors of the power applicator may be embedded in the surface of the chamber, may lie against the surface of the chamber, or may be spaced and free-standing from the chamber. Preferably the current-carrying conductors are free-standing and spaced from the chamber to permit easy placement and removal of the chamber within the applicator. Such an arrangement permits an applicator to be conveniently used sequentially with multiple chambers. When the current-carrying conductors are spaced from the chamber, they preferably are within about 1 cm(1/2"), more preferably within about 0.25 cm (1/10"), from the outer chamber wall and configured to the shape of the chamber.

Although it is preferred that the conductor loops completely encircle the chamber, we have also successfully practiced the invention with conductors passing through the container, e.g., with the length 24a of the conductors 24 passing through the center of the chamber and perpendicular to the longitudinal axis of the chamber. A plasma sheath was generated within the chamber between the conductors and the sidewall of the chamber that lies within the conductor loop.

The applicator produces a high-frequency magnetic field that extends through the chamber parallel to the longitudinal axis. Charged species existing within the gaseous contents of the chamber, initiated for example by the electric field penetrating into the chamber, respond to the high-frequency magnetic field such that a current loop transverse to the longitudinal axis is induced within the gaseous material. The induced current loop forms near the boundary of the chamber and is of lesser magnitude the greater its distance from the chamber wall (as understood in the art, the induced currents are oriented so that their associated magnetic fields partially reduce the magnetic field produced by the current-carrying means, this progressively reduces the field strength the greater the distance from the chamber wall). Work done by

the induced plasma current loop intensifies the ionization and
dissociation of the gaseous species, producing an intense
plasma sheath that conforms to the interior of the chamber
wall. This plasma sheath extends laterally in the axial
direction, because of the axially-extending nature of the
power applicator, and because of the low pressures typically
existing in the chamber. The plasma covers the sidewalls of
the chamber inside of the applicator bounds. At planar
chamber walls a rather planar plasma sheath parallel to the
chamber wall is formed, and at curved chamber walls a plasma
sheath that follows the curved surface is formed.

Once formed, the induced current loop becomes the
dominant mechanism by which the applied high-frequency power
is transferred to the plasma. Increased power can be applied
to cause increased dissociation and ionization.

The condition in which an intense plasma is formed by
the induced current loop is termed magnetically induced
ionization. Typically, there is a sharp increase in luminosity
of the plasma as magnetically induced ionization occurs, and
there is a visible difference in luminosity from the chamber
wall toward the center of the chamber.

FIG. 3a is a sectional view through the chamber 10⁻ taken
during operation of the apparatus. The dots in the drawing
represent the magnetically induced plasma within the chamber
(actually the plasma is observed by its visible luminosity).
As seen, the plasma is more intense or dense at its outer
boundary adjacent the chamber sidewalls, and gradually
declines in intensity the greater its distance from the
sidewall. At some distance, the intensity may decline to an
extent that there is hardly any visible luminosity. Plasma
intensities of 10^{12} electrons per cubic centimeter have been
reported in the literature for magnetically induced
ionizations, in contrast to electron densities of 10^{10}
electrons per cubic centimeter reported for plasmas generated
through so-called capacitive coupling; the latter occurs, for
example, when an electric field penetrates into the chamber of

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an apparatus of the invention and acts on the neutral gaseous
contents of the chamber, e.g., during plasma initiation prior
to achieving magnetically induced ionization.

As shown in Figure 3a, when gases are introduced into the
chamber through a central inlet tube, they first diffuse
through the relatively lower-density plasma to the higher-
density plasma sheath. Such a path for the gas is considered
advantageous, for example, to facilitate formation of carbon
monoxide when vaporized water/alcohol mixtures are used, as
shown in earlier patent applications 07/787,891, filed
November 5, 1991; 08/861,291, filed May 14, 1993; and
08/151,184, filed November 12, 1993. These patent
applications, and a published PCT counterpart (WO 93/08927,
published May 13, 1993) are hereby incorporated by reference.

The intense plasma has many benefits. For example, it
produces rapid dissociation of diamond-precursor gaseous
feedstocks so as to allow rapid deposition of diamond films.
The conformance and proximity of the plasma sheath to the
chamber wall, where diamond deposition occurs, is advantageous
because dissociated·diamond-forming species need travel only a
short·distance to contact the work surface. The high
temperatures and high electron density produced in an intense
plasma can be also used in other ways, such as to clean
surfaces, etch surfaces, or to incinerate waste materials.

As previously noted, the sidewalls of the chamber can be
used as a work surface, or a work surface can be supported on
and generally conform to the chamber sidewalls. Thus, the
work surface is preferably disposed at and conforms to the
outer boundary of the plasma sheath, where the plasma sheath
is most intense and active; and the generally extensive work
surface, preferably planar, is acted upon by the plasma sheath
at this high intensity over substantially the full extent of
the work surface. Large-area films can be deposited, or
large-area surfaces cleaned, etched. etc. Work surfaces can
also be located at other places in the plasma sheath, though
they generally extend in the direction of the longitudinal

axis and preferably have a shape conforming to the contour of the plasma sheath.

The power supply to the applicator generally may be any type known to those skilled in the art. The desired power level varies with the pressure in the chamber and the ionization potential of the gas in the chamber; the type of deposition, etching, or cleaning, or other operation to be carried out; the rate of throughput desired; the temperature ranges appropriate for materials and substrates being used, etc. The needed power to induce ionization can readily be determined in many cases from reported relationships between power level, pressure, and desired gases; and simple experimentation can be used by general principles reported in the field of induction arcs for nonreported materials or to further define the needed and preferred conditions.

For diamond deposition using water-ethanol mixtures, power levels of about 7 watts or more per square centimeter have been sufficient to deposit diamond at a rate of about 1μm/hr. Power density is calculated by dividing the power dissipated in the chamber by the area of the longitudinally extending sidewalls of the chamber (the power dissipated in the chamber can be measured, or it can be calculated with rather good accuracy by multiplying the initial applied dc power by the efficiency of the applicator, which for the illustrated applicator is generally on the order of 65 percent. While not rigorous, other diamond-forming feedstocks such as hydrogen-methane mixtures generally require power densities approximately twice as great.   At gas pressures less than 0.5 Torr, magnetically induced ionization is generally achieved with power densities of two or three watts per square centimeter of chamber sidewall .

RF power supply units are commercially available for example, from Lepel Corporation (e.g., Model NO. T-40-3-DF4-TL). Schematic diagrams of other useful rf power supplies are shown in FIGS. 4 and 6. FIG. 4 shows a rf power supply 30 which provides variable coupling control. The rf power supply

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comprises a high voltage variable DC power source 31 connected
through rf choke coil 32 to the plate of vacuum tube 33. The
switching on and off converts the dc supply energy to high-
frequency energy. Vacuum tube 33 is connected to grid
complex-impedance circuit 35, and primary tank coil 36, which
has variable tank capacitance. Primary tank coil 36 and
coupling-link coil 37 comprise the matching network. The
coupling-link coil 37 is connected between the bus bars 38 and
39, which are connected to the conductor loops 24 and
capacitor bank 26.

FIG. 6 diagrams another rf power supply having a direct
coupled circuit 40. The circuit comprises a transformer 41
from which an auxiliary 44 source supplies source energy to
the oscillator filament. Inductor 42 and capacitor 43 form a
decoupling circuit through which dc energy is fed at 31.
Meter 45, resistor 46, rf choke inductor 47, variable
capacitor 48, and inductor 49 comprise a grid circuit complex
impedance.. Vacuum tube 51 switches the dc supply at high
frequency and pumps rf current to the capacitors 26 and
current-carrying conductors 24 through bus bars such as 38 and
39 in FIG. 4. The connection 52 to ground affords a dc return
path from the vacuum tube to the power supply.

The power supply provides a high frequency current to the
applicator, by which is meant herein a frequency between about
60 Hz and 100 MHz, where induction-coupled plasmas have been
operated using other applicators and applicator geometries.
The power supply preferably operates at about 0.5 to 20 MHz,
more preferably at about 7 to 15 MHz. Such frequencies are
within the band commonly referred to as a radio frequency.
Government regulators have allotted 13.56 MHz for industrial
uses, and that is a suitable frequency for use in the
invention.

Various feed stocks may be supplied to the chamber
depending on the function to be performed, for example,
deposition of diamond or other materials, etching, cleaning,
or pyrolysis. The feedstock is generally gaseous, or

vaporizes to a gaseous form upon introduction into the chamber. Suitable diamond-forming feedstock gases include a mixture of alcohol and water. Alcohols suitable for use in the invention include methanol, ethanol, and isopropanol. Ethanol is a particularly preferred alcohol. The ratio of alcohol to water is preferably in the range of about 1:1.5 to 4:1, more preferably in the range of about 1:1 to 2:1, most preferably 1:1 to 1.2:1.

For depositing films other than diamond, silane-containing feedstocks can be used with oxygen for SiO_2 deposition, with nitrogen for Si_3N_4 deposition, and with methane for SiC deposition; or proportionate mixtures can be used for various silicon alloys.

For etching or priming, i.e., removal of surface material, the gas choice is highly dependent of the surface to be etched. For silicon surfaces, molecular H_2 can be used as well as CF_4/O_2 mixtures. For polymeric surfaces, oxygen-rich gases such as O_2, H_2O, N_2O or H_2O_2 can be used.

For cleaning of substrate surfaces to remove residual carbon, oil, or adhesive, oxygen-based feedstocks such as O_2, H_2O, N_2O or H_2O_2 would also be suitable.

When the apparatus of the current invention is used for hazardous waste destruction, the hazardous material must present itself in vapor form or be entrained in a process gas stream. For example, destruction of trichloroethylene can be performed by entraining the liquid in a gas stream containing O_2 and H_2. The resultant gas stream would contain CO, HCl, and H_2O. The HCl and H_2O would be condensed from the gas stream and neutralized. The CO would be burnt to CO_2.

The invention will be further illustrated by the following examples.

Example 1

A polycrystalline diamond film was produced using a chamber as generally shown in Figure 1 and an applicator generally as shown in Figure 4. The dome portion 14 of the

chamber was made of quartz with a wall thickness of 3/8 inch
(approximately 1 centimeter) and an area at its base of 14
inches by 16 inches (about 35 by 40 cm); and the base plate
had a thickness of 1.25 inches (about 3 centimeters).

An array of eighteen conductor loops was used, with the
conductors being 1.27-cm diameter copper tubes and having a
"U" shape, with 53-cm long legs (24b in FIG. 4) and a 18-cm
base (24a in FIG. 4). A capacitor bank comprising eleven 250-
pf, 30 kV (test voltage) capacitors, providing a total
capacitance of 2750-pf, was used, and the circuit was operated
to resonate at 8 MHz.

Three quartz substrate plates, one 8 inches by 10 inches
(20 by 25 cm) in area and two 4 inches by 4 inches (10 by 10
cm) in area, were laid on the base plate of the apparatus to
cover an area 8 inches x 14 inches (20 by 35 cm). The
substrate plates had been sandblasted and subsequently
rescratched using a paste containing diamond particles
averaging one micrometer in diameter. The chamber was
evacuated, and a mixture of water vapor and ethanol vapor
introduced into the chamber through the tube 18. The water
vapor was introduced at a flow rate of 19 sccm and the ethanol
vapor at a flow rate of 15 sccm. Pressure in the chamber
was set at 0.4 Torr. The plasma power supply was activated
and a plasma initiated, whereupon the pressure in the chamber
was increased to 0.5 Torr. A dc voltage of 6.4 kV was applied
to the plate of the power tube 33, resulting in a plate
current of 1.5 A at a frequency of 8.5 MHz. The plasma power
density was calculated as about 3 watts per square centimeter
of internal sidewall surface area of the chamber. The system
was operated steadily for 47 hours at which time the power was
discontinued, the system vented, and the samples removed from
the chamber. Visual inspection of the plates showed that
diamond film had been deposited over essentially the whole 8"
x 14" area. Some gradations in the thickness of the deposited
film, visible as different shades, were detected; but large
portions of the deposit were of a rather uniform thickness.

The samples were subjected to Raman spectroscopy and a
pronounced peak at 1332 cm^{-1} was detected. SEM photographs
through a cross section of the sample revealed a thickness of
about 30 microns over substantial portions of the deposit, and
microscopic examination of the top surface of the film
revealed faceting of the film.

Example 2

A polycrystalline diamond film was produced using
apparatus as shown in Figure 3 (except that the inlet tube 18´
was coaxial with and within tube 19´ as illustrated for
chamber 10 in Figure 1) and an applicator generally as shown
in Figure 4.   The chamber comprised a flat base plate 12´ of
quartz that was 0.375 inch (1 cm) thick and approximately 10
inches (25 cm) long and 5 inches (12.5 cm) wide. . The dome
portion 14´ was cut from a cylinder having a diameter of
approximately 6 inches (15 cm), cut along a 5-inch (12.5-cm)
chord of the cylinder. The wall thickness was about 0.125
inch (0.32 cm).

An array of eighteen conductor loops was used, with the
conductors being 1.27 -cm diameter copper tubes and having a
"U" shape, with 53 -cm long legs (24b in FIG. 4) and a 18-cm
base (24a in FIG. 4). A capacitor bank comprising eleven
250-pF, 20 kV capacitors, providing a total capacitance of
2750 pF was used, and the circuit was operated to resonate at
8.5 MHz.

Two silicon wafers, approximately five inches (10 cm)
in diameter, were inserted into the chamber and laid on the
base plate. The chamber was evacuated and a mixture of water
vapor and ethanol vapor introduced using a flow rate of 8 sccm
for the water vapor and 12 sccm for the ethanol vapor. The
power supply was activated and a plasma initiated, and
pressure inside the chamber established at 0.7 Torr. The dc
voltage to the plate of the power tube was set at 7.3 kV
producing a plate current of 1.8 A at a frequency of 8.5 MHz.
These conditions were maintained for 120 hours. Thereupon,

the voltage supply was discontinued, the system vented, and
the silicon wafers removed from the chamber. Diamond film had
deposited on the silicon wafers, and also on the inside
surface of the dome area of the chamber.

The material on the inside dome surface was released from
an area about 8 inches by 8 inches (20 cm by 20 cm). SEM
showed this material to be well faceted at a thickness of
about 70 μm. Raman spectroscopy showed a well-defined 1332
cm^{-1} peak on a strong luminescent background. Material taken
from the silicon wafers showed a better Raman spectrum with a
sharper peak and very little background luminescence.
Interestingly, the diamond on the silicon wafer was
substantially thicker, probably due to the higher substrate
temperature resulting from the silicon wafer resting on the
flat plate section which was thicker than the dome.

Example 3

Apparatus similar to that as described in Example 2 was
used to etch a silicon wafer, except that fewer conductor
loops were used and the total capacitance was 1000-1500 pF.
The wafer was placed on the base plate of the chamber and the
chamber pumped down to less than 0.050 Torr. Hydrogen was
introduced into the chamber through a mass flow controller at
a rate of 40 sccm, after which the power supply was activated
and the plasma initiated. The pressure was established at
0.124 Torr, and the dc voltage to the plate of the power tube
was set at 3.2 kV, producing a plate current of 0.8 amps at a
frequency of 13.56 MHz. An optical emission spectrum was
taken during the plasma treatment through the quartz dome.
The emission spectrum showed peaks for atomic hydrogen at 656
and 486 nanometers, and in addition, showed a sizable emission
at 414 nanometers, which indicates the presence of SiH
generated during the etching process. Treatment was continued
for 3 hours and 40 minutes, whereupon the voltage was
discontinued, the system vented, and the silicon wafer removed
from the chamber. A visible change had occurred in the finish

of the wafer.   Examination by SEM micrographs showed that the
silicon surface had been pronouncedly etched by the hydrogen
plasma exposure.

Example 4

    Apparatus as described in Example 3 was used to clean a
5-inch diameter silicon wafer which had been sprayed with 3M
"Super 77" Spray Adhesive and allowed to dry.   The thickness
of the layer was about 500 μm.   The wafer was cut in two and
one-half placed into the chamber resting on the base plate.
The chamber was evacuated to 0.005 Torr and water vapor
introduced into the chamber through a needle valve until the
pressure read .0.050 Torr. The power supply was activated and a
plasma initiated.   DC voltage of 3 kV was supplied to the
plate of the vacuum tube, producing a plate current of 0.75
amps.   Initially, for about two minutes, the system pressure
spiked as adhesive was being dissolved.   The pressure spike
caused the plasma to extinguish and then restart when the
pressure returned to the initial low pressure level.   The
system pressure stabilized in about two minutes at a pressure
of 0.045 Torr; the plate voltage was 2.5 kV, and the plate
current, 0.75 amps.   The system was then run for about five
minutes, whereupon the voltage supply was discontinued, the
system vented, and the wafer removed from the chamber.' After
inspection it could be seen that cleaning was not complete;
only the central section of the wafer had been cleaned.
Treatment was then resumed with water introduced to give a
pressure of 0.070 Torr prior to plasma initiation and a
pressure of 0.119 Torr after plasma initiation.   The plate
voltage was 3 kV and current on the plate was 1 amp.
Treatment was continued for 15 minutes whereupon the glue
appeared to have been dissolved, but a residue was still
apparent on the wafer.   The sample was reloaded and treatment
repeated for 15 minutes, with a pressure of 0.130 Torr, plate
voltage of 3.5 kV and current of 0.8 amps.   After 15 minutes
the treatment was discontinued and the sample removed and

inspected.   Some residue present as a fine powder was present
but was easily removed by wiping the surface of the wafer with
a wet cloth.

Obviously, numerous modifications and variations of the
present invention are possible in light of the above
teachings.   It is therefore to be understood that within the
scope of the appended claims, the invention may be practiced
otherwise than as specifically described herein.

CLAIMS:

1.   A method for treating a substrate with a plasma comprising

a)   providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis;

b)   providing an axially-extending array of current-carrying conductors that at least partially encircle the chamber and are substantially transverse to the longitudinal axis of the chamber;

c)   providing a gaseous material in the chamber;

d)   providing high-frequency current in the conductors to magnetically induce ionization of the gaseous material in the chamber and form a plasma sheath that surrounds and extends along the longitudinal axis and conforms to sidewalls of the chamber; and

e)   exposing to the plasma sheath a work surface that extends in the direction of the longitudinal axis.

2.   A method of claim 1 in which the current-carrying conductors comprise loops electrically connected in parallel.

3.   A method of claim 1 in which at least one sidewall of the chamber is planar, and the plasma sheath extends as a planar sheath parallel to the planar sidewall.

4.   A method of claim 3 in which the planar sidewall is at least 100 cm^2 in area and the plasma sheath extends over the planar sidewall.

5.   A method of claim 3 in which the planar sidewall is at least one square meter in area.

6.   A method of claim 1 in which the gaseous material forms a material in the plasma sheath that etches the work surface.

7.   A method of claim 1 in which the gaseous material forms a material in the plasma sheath that cleans the work surface of material coated on the work surface.

8.   A method for treating a substrate with a plasma comprising:

a)   providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis and extend parallel to the longitudinal axis, at least one sidewall being planar;

b)   providing an axially-extending array of current-carrying conductor loops that encircle the planar sidewall, are substantially transverse to the longitudinal axis, and are electrically connected in parallel;

c)   providing a gaseous material in the chamber;

d)   providing high-frequency current in the conductor loops to magnetically induce ionization of the gaseous material in the chamber and form a plasma sheath that surrounds and extends along the longitudinal axis and conforms to sidewalls of the chamber, a portion of the plasma sheath extending as a planar sheath parallel to the planar sidewall; and

e)   exposing to the planar plasma sheath a work surface that extends in the direction of the longitudinal axis.

9.   A method of claim 8 in which the planar sidewall is at least 100 cm² in area and the planar sheath extends over the planar sidewall.

10.   A method of claim 8 in which the planar sidewall is at least one meter square in area and the planar plasma sheath extends over the planar sidewall.

11.   A method of claim 8 in which the gaseous material forms a material in the plasma sheath that etches the work surface.

12 . A method for forming diamond film comprising:

a)   providing a chamber having a longitudinal axis and sidewalls that at least partially surround the longitudinal axis;

b)   providing an axially-extending array of current-carrying conductors that encircle the chamber and are substantially transverse to the longitudinal axis of the chamber;

c)   providing a gaseous diamond-precursor feedstock in the chamber;

d)   providing high-frequency current in the conductors to magnetically induce ionization of the gaseous material in the chamber and form a plasma sheath that surrounds and extends along the longitudinal axis and conforms to sidewalls of the chamber; and

e)   exposing to the plasma sheath a work surface that extends in the direction of the longitudinal axis and is adapted for diamond film deposition.

13.   A method of claim 12 in which the current-carrying conductors are electrically connected in parallel.

14.   A method of claim 12 in which at least one sidewall of the chamber is planar, and the plasma sheath extends as a planar plasma sheath parallel to the planar sidewall of said chamber.

15.   A method of claim 14 in which the work surface is planar and is parallel to and exposed to the planar plasma sheath.

16. A method of claim 15 in which the planar work surface is at least 100 cm² in area and the planar plasma sheath extends over the planar work surface.

17. A method of claim 15 in which the planar work surface is at least one square meter in area and the planar sheath extends over the planar work surface.

18. A method for forming diamond film comprising:

a) providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis and extend parallel to the longitudinal axis, at least one sidewall being planar;

b) providing an axially-extending array of current-carrying conductor loops that individually at least partially encircle the chamber, are substantially transverse to the longitudinal axis, and are electrically connected in parallel;

c) providing a gaseous diamond precursor material in the chamber;

d) providing high-frequency current in the conductor loops to magnetically induce ionization of the gaseous material in the chamber and form a plasma sheath that surrounds and extends along the longitudinal axis and conforms to the sidewalls of the chamber, a portion of the plasma sheath extending as a planar sheath parallel to the planar sidewall; and

e) exposing to the plasma sheath a work surface that extends in the direction of the longitudinal axis.

19. A method of claim 18 in which the planar sidewall is at least 100 cm² in area, and said work surface is exposed to said planar portion of said plasma sheath.

20. A method of claim 18 in which the planar sidewall is at least one meter square in area, and said work surface is

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exposed to said planar portion of said plasma sheath at an outer boundary of the planar portion of the plasma sheath.

21. A plasma treatment apparatus comprising:

a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis, at least one sidewall being an extensive planar wall that is parallel to the longitudinal axis;

means for providing a gas into the chamber;

an axially extending array of current-carrying conductor loops that encircle the chamber, are substantially transverse to the longitudinal axis, and establish a magnetic field parallel to the longitudinal axis of the chamber; and

a power supply connected to the conductor array and adapted to provide high frequency current in the conductor loops to magnetically induce ionization of the gaseous material in the chamber.

22. Apparatus of claim 21 in which the individual conductor loops are electrically connected in parallel.

23. Apparatus of claim 21 in which the conductor loops comprise at least in part cooled tubes.

24. A method for treating a work surface with a plasma, comprising:

a)   providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis;

b)   providing a gaseous material in the chamber;

c)   generating within said chamber a magnetically induced plasma sheath that surrounds and extends along the longitudinal axis and conforms to the sidewalls of the chamber; and

d)   positioning the work surface to extend in the
direction of the longitudinal axis of the chamber and exposing
the work surface to said plasma sheath.

25.   The method of claim 24, wherein step d) of
positioning the work surface includes exposing the work
surface to the outer boundary of the plasma sheath.

26.   The method of claim 24, wherein said step c) of
generating a plasma sheath comprises:

    generating high-frequency electric current in a loop that
at least partially encircles the chamber and is substantially
transverse to the longitudinal axis of the chamber, the high-
frequency current generating a magnetic field within the
chamber in a direction parallel to the longitudinal axis and
with a magnitude sufficiently great to magnetically induce
ionization of the gaseous material in the chamber.

27.   The method of claim 26, wherein the high-frequency
current is generating in an axially extending array of
current-carrying conductors that at least partially encircle
the chamber.

28.   The method of claim 26, wherein the array comprises
individual conductors encircling the chamber and electrically
connected in parallel.

29.   The method of claim 24, wherein said step d) comprises:

etching the work surface.

30.   The method of claim 24, wherein said step d) comprises:

cleaning the work surface.

31.   The method of claim 24, wherein:

said step b) comprises providing a gaseous diamond-precursor feedstock in the chamber; and

said step d) comprises depositing a diamond film on said work surface.

32.   The method of claim 24, wherein said work surface comprises a planar surface that is at least 100 cm^2 in area.

33.   The method of claim 25, wherein said work surface comprises a planar surface that is at least 100 cm^2 in area.

34.   The method of claim 29, wherein said work surface comprises a planar surface that is at least 100 cm^2 in area.

35.   The method of claim 30, wherein said work surface comprises a planar surface that is at least 100 cm^2 in area.

36.   The method of claim 31, wherein said work surface comprises a planar surface that is at least 100 cm² in area.

37.   The method of claim 24, in which the chamber comprises at least two parallel planar sidewalls.

38.   A method for treating a work surface with a plasma, comprising:

a)   providing a chamber having a longitudinal axis and sidewalls that surround the longitudinal axis, said chamber dimensioned such that when the longitudinal axis is aligned with a time varying magnetic field, the chamber and field will support a plasma sheath having characteristics suitable for performing a predetermined plasma treatment on the workpiece;

b)   providing a gaseous material in the chamber;

c)   generating within said chamber a time varying magnetic field to induce magnetically a plasma sheath that surrounds and extends along the longitudinal axis and conforms to the sidewalls of the chamber, said magnetic field having a radial intensity distribution such that magnetic flux linked by said plasma sheath is sufficient to induce a circumferential electric field in the plasma sheath sufficient to sustain a plasma of an energy density requisite to perform said predetermined plasma treatment; and

d)   positioning the work surface nominally parallel to the time-varying magnetic field and at a distance from the
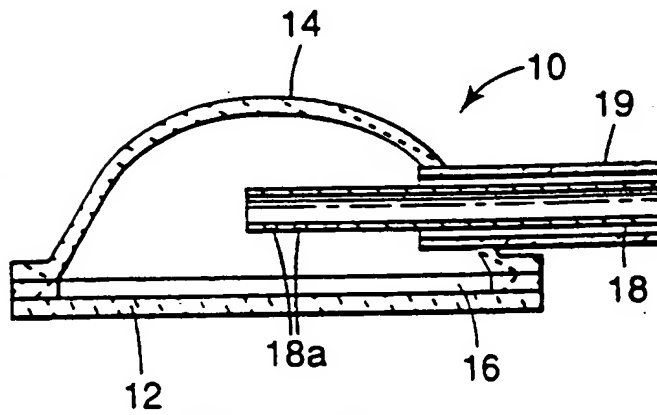
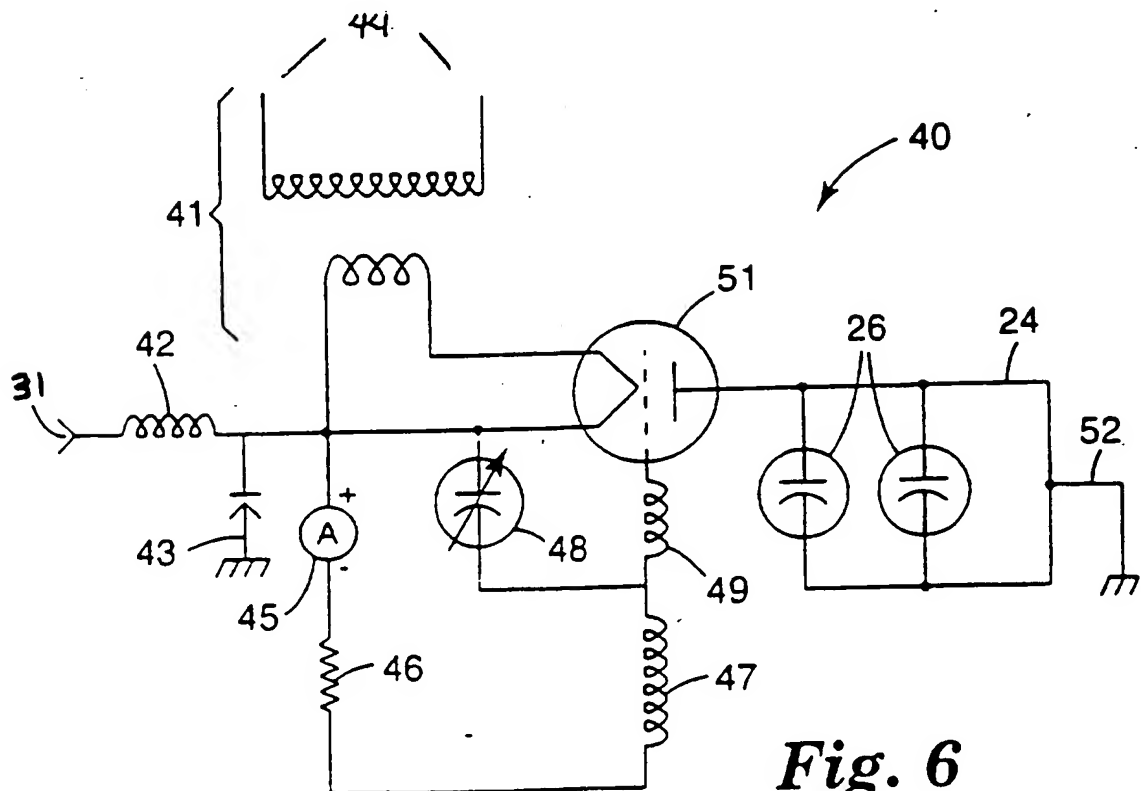plasma sheath appropriate and performing the predetermined

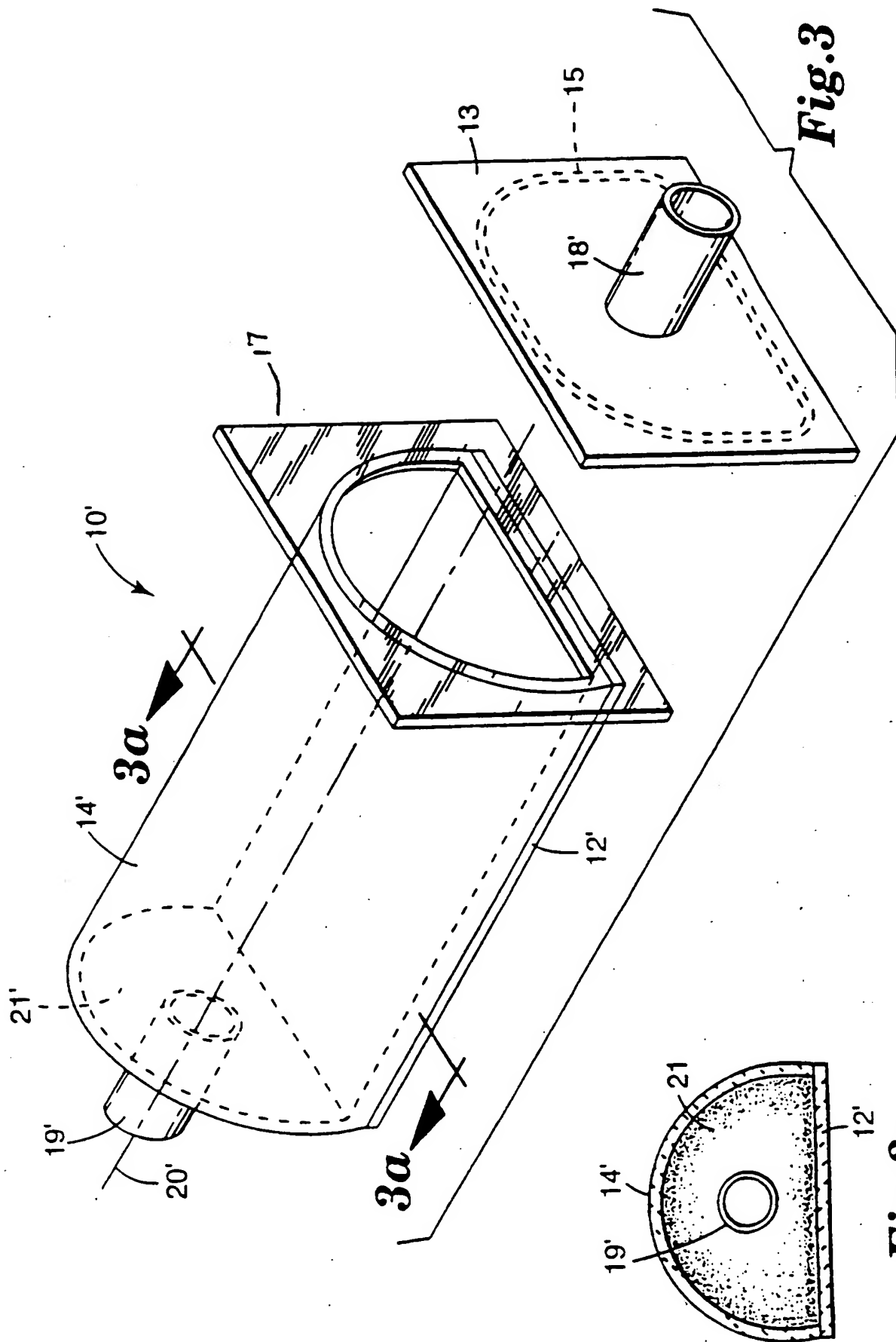plasma treatment.
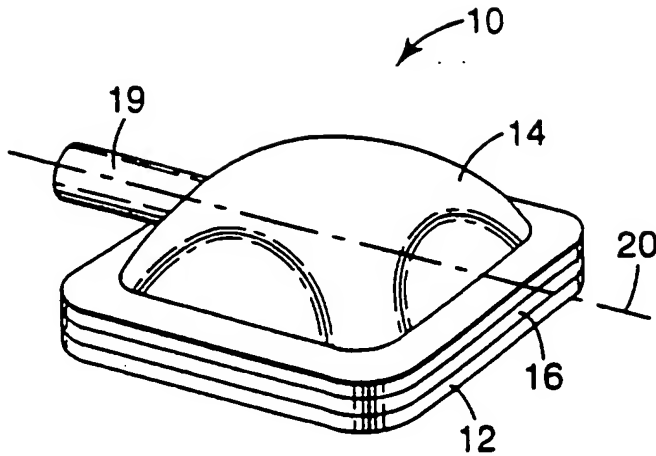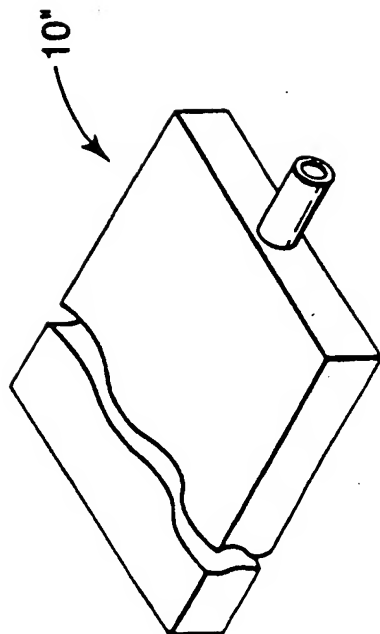
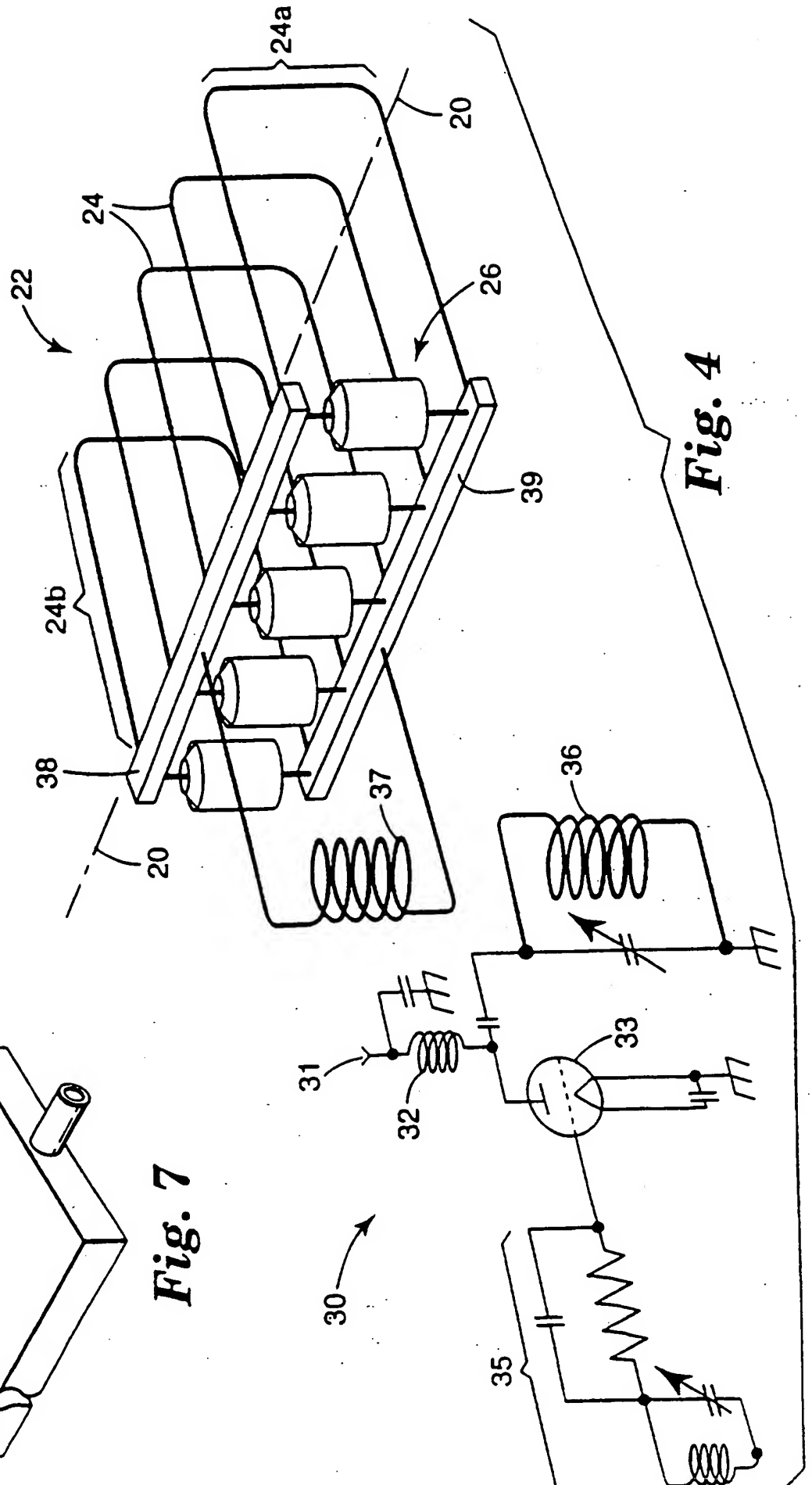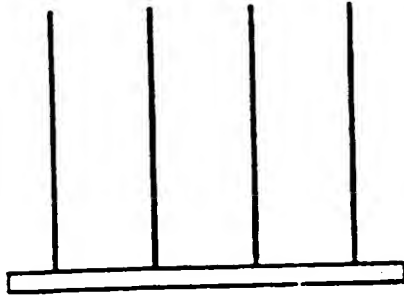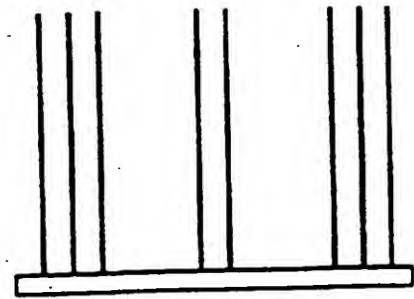**Fig. 1**
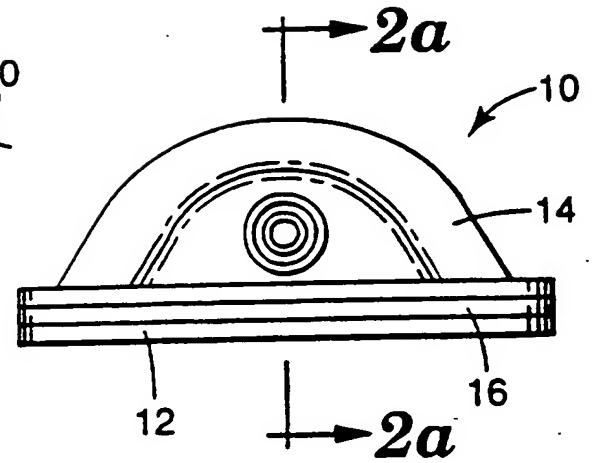
Fig. 2

Fig. 2a

Fig. 6

Fig.3

Fig.3a

Fig. 4
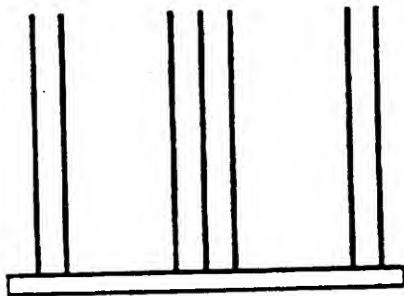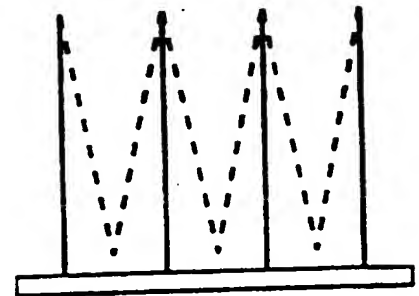
Fig. 7

Fig. 5a
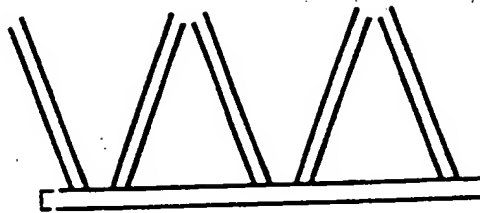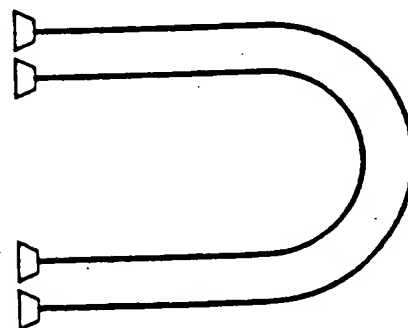
Fig. 5b

Fig. 5c

Fig. 5d

Fig. 5e

Fig. 5f

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H05H 1/02; C23F 1/00; C03C 15/00, 25/06; C23C 16/00
US CL :427/571, 577; 216/68; 118/7231, 724

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/569, 571, 575, 577; 216/68, 69, 70, 71; 118/7231, 724

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 3,677,799 (HOU) 18 July 1972; See Fig. 1 and 1A; Abstract; Summary; col. 4, lines 49-56, 64-75; col. 5, lines 46-58; col. 6, lines 28-58; and col . 7, lines 55-58.	1-2, 24, 26, 28, 38 -------------- 3-23, 25, 32-37
X ---- Y	US, A, 5,275,798 (AIDA) o4 January 1994; See Abstract; Fig. 1; col. 3, lines 28-49; col. 4, lines 15-36; and col. 5, line 61-col. 6, line14.	24, 26-27, 29-31 ---------- 1-23, 32-38
X	US, A, 4,824,690 (HEINECKE et al) 25 April 1989; See Abstract; Figure; col. 2, lines 1-32 and 42-51; col. 3, lines 37-39; and claims 1-2.	24-30, 38

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US, A, 5,431,968 (MILLER et al) 11 July 1995; See Figures; Abstract; col. 3, line 64-col. 4, line 45; col. 5, lines 21-54; and col. 6, lines 1-20 and 41-50.	1-38
Y	US, A, 4,690,793 (HITACHI, LTD., et al) 01 September 1987; See Fig. 1 and col. 6, lines 18-40	3-5, 8-11, 14-22, 33-37
Y	US, A, 4,772,486 (ISHIHARA et al) 20 September 1988; See Figure 1 and examples 1-3	3-5, 8-11, 14-22, 32-37
Y	ECKERT, "The Induction Arc: A State-of-the-Art Review", High Temperature Science 6, pp99, 525-526; See p 99, Introduction	3-5, 8-11, 14-22, 32-37
Y	US, A, 3,843,392 (STERLING et al) 22 October 1974; See Figure and col. 2, lines 40-51	24, 26-27, 38
X	RUDDER, "Development of Large-Area RF Induction Plasma for Cost Effective Diamond CVD", Technical Proposal, Research Triangle Institute, May 1993, pp1-84; See pp 6-11	1-22, 24-38
Y	US, A, 5,277,751 (OGLE) 11 January 1994; See Abstract and Figures	3-5,8-11,14-22, 32-37
Y	US, A, 5,261,962 (HAMAMOTO et al) 16 November 1993; See Abstract and Figures	3-5, 8-11, 14-22, 32-37
X	US, A, 4,673,589 (STANDLEY) 16 June 1987; See Abstract and Figures	24, 26-27, 38
X	US, A, 4,212,933 (mARKIN et al) 15 July 1980; See Abstract and Figures	24, 26-27, 38
X	US, A, 4,298,629 (NOZAKI etal) 03 November 1981; See Abstract and Figures	24, 26-27, 38
X	US, A, 4,686,113 (DELFINO et al) 11 August 1987; See Abstract and Figures	24, 26-27, 38
A	US, A, 5,346,578 *BENZING et al) 13 September 1994; See Figures 1, 3-5; col. 4, lines 40-60; and col. 6, line 58- col. 7, line 50	1-38
A,P	US, A, 5,401,350 (PATRICK et al) 28 March 1995; See Abstract and Figures	1-38

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BARNS et al, "Electron Energy Distribution Function Measurements in a Planar Inductive Oxygen Radio Frequency Glow Discharge", Appl. pHYS. lETT, 62(21), 24 mAY 1993, PP 2622-2624	1-38
A	HOPWOOD et al, "Electromagnetic Fields in a Radio-Frequency Induction Plasma" J. Vac. Sci. Technol. A 11(1), January/February 1993, pp 147-151	1-38

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT ·